

# CHAPTER 4

## NONLINEAR OPTICAL SUSCEPTIBILITIES AND HYPERPOLARIZABILITY OF BORATE $\text{LiNaB}_4\text{O}_7$ NONCENTROSYMMETRIC SINGLE CRYSTALS

The borate  $\text{LiNaB}_4\text{O}_7$  single crystal was synthesized by employing high-temperature reaction methods. The purity of the sample was checked by x-ray powder diffraction. The optical properties were measured by analyzing the diffuse reflectance data which showed a band gap of about 3.88 eV. Linear and nonlinear optical susceptibility calculations have been performed using the all-electron full potential linearized augmented plane-wave method using four different exchange correlation potentials. It was found that, the title compound possesses an optical gap of about 2.80 eV using the Local Density Approximation (LDA), 2.91 eV by Generalized Gradient Approximation (GGA), 3.21 eV for the Engel-Vosko Generalized Gradient Approximation (EVGGA) and 3.81 eV using modified Becke-Johnson (mBJ) potential. This compares well with our experimentally measured energy band gap of 3.88 eV. Our calculations show that, EVGGA, and mBJ cause a blue spectral shift with significant changes in the whole spectra. The observed spectral shifts are in agreement with the calculated band structure and corresponding electron density of states. The tensor  $\chi_{ijk}^{(2)}$  describes the second-order nonlinear optical effect and the symmetry allows only five non zero component namely; the 113, 232, 311, 322 and 333 components with 322 being the dominant one with a value 0.15 pm/V ( $d_{32}=0.0733$  pm/V) at static limit and 0.16 pm/V ( $d_{32}=0.0795$  pm/V) at  $\lambda=1064$  nm. For the dominant component the microscopic second order hyperpolarizability,  $\beta_{322}$ , was found to be  $\beta_{322}$ ,  $0.306 \times 10^{-30}$  esu at static limit and  $0.332 \times 10^{-30}$  esu at  $\lambda=1064$  nm.

## 4.1 HISTORICAL REVIEW

Borate materials have been extensively investigated because of their potential applications in Nonlinear Optics (NLO) and laser engineering and because they show excellent properties such as short growth period, large effective nonlinear coefficient, high damage threshold, and good mechanical properties. For example,  $\text{BaB}_2\text{O}_4$ ,  $\text{LiB}_3\text{O}_5$ ,  $\text{CsB}_3\text{O}_5$ , and  $\text{YCa}_4(\text{BO}_3)_3\text{O}$  are all well-known NLO crystals [1]. As a result of their complicated crystal structures borates are among the most interesting and therefore the most extensively studied materials. Since 1962, when the binary phase diagram  $\text{Bi}_2\text{O}_3$ - $\text{B}_2\text{O}_3$  was investigated, many methods of obtaining the borate crystals were found and described in detail [2-7]. In the  $\text{Bi}_2\text{O}_3$ - $\text{B}_2\text{O}_3$  system [8], at least five compounds have been proposed and structurally characterized. They are  $\text{Bi}_{24}\text{B}_2\text{O}_{39}$  [9],  $\text{Bi}_4\text{B}_2\text{O}_9$  [10],  $\text{Bi}_3\text{B}_5\text{O}_{12}$  [11],  $\text{BiB}_3\text{O}_6$  [12], and  $\text{Bi}_2\text{B}_8\text{O}_{15}$  [13]. Among them,  $\text{Bi}_4\text{B}_2\text{O}_9$  was reported to have high double refraction [14];  $\text{Bi}_3\text{B}_5\text{O}_{12}$  displays stimulated Raman scattering and luminescence properties [15,16].  $\text{BiB}_3\text{O}_6$  is the most extensively studied because it has been established as a NLO material with promising physical properties and has furthermore been characterized in detail with respect to their piezoelectric, pyroelectric, dielectric, elastic, and thermoelastic properties [17].

It was established that borate crystals, in particular  $\text{BiB}_3\text{O}_6$ , exhibit high NLO susceptibilities [18-21], particularly for Second Harmonic Generation (SHG) and Third Harmonic Generation (THG) applications. Theoretical examinations have shown that, anionic groups and chemical bonding structures of boron atoms have a major influence on the nonlinear properties of these crystals [22, 23]. It is reasonable to emphasize that, other interesting materials may also be found in more complex borates incorporating bismuth together with other cationic elements. Based on this idea, several ternary (quaternary) bismuth-containing borates that crystallize in the noncentrosymmetric space groups have been recently synthesized, including  $\text{BaBiBO}_4$ ,  $\text{Bi}_2\text{ZnB}_2\text{O}_7$ ,  $\text{CaBiGaB}_2\text{O}_7$ ,  $\text{Bi}_2\text{CaB}_2\text{O}_7$ , and  $\text{Bi}_2\text{SrB}_2\text{O}_7$  [24-26].

Further insight into the electronic structures and the physical properties of materials can be obtained from the calculations of interband optical functions. The considered compound is particularly interesting for its NLO properties, which could be related to the anionic and cationic polyhedral